

518 Rec'd PGT/PTO 31 JUL 2001

FORM PTO-1390
(REV 10/95)

U. S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

HUBR 1192 (10106132)

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

UNKNOWN 09/890544

INTERNATIONAL APPLICATION NO.

PCT/EP00/00900

INTERNATIONAL FILING DATE

04/02/00

PRIORITY DATE CLAIMED

06/02/99

TITLE OF INVENTION

METHOD FOR PRODUCING SODIUM DICYNAMIDE

APPLICANT(S) FOR DO/EO/US

Franz Thalhammer, Helmut Tautz

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is the FIRST submission of items concerning a filing under 35 U.S.C. 371.
 2. ☐ This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
 3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(l).
 4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
 5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau.)
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
 6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)) is attached hereto.
 7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
 8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
 9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
 10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).
- Items 11. to 16. below concern document(s) or information included:
11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
 12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
 13. ☒ A FIRST preliminary amendment.
 - ☐ A SECOND or SUBSEQUENT preliminary amendment.
 14. ☐ A substitute specification.
 15. ☐ A change of power of attorney and/or address letter.
 16. ☐ Other items or information: (a) International Search Report; (b)
 17. ☐ The follow fees are submitted: (a) Check for Filing Fee

EXPRESS MAIL NO. EL 649537808 US

09/890544

JC05 Rec'd PCT/PTO 3 1 JUL 2001

BASIC NATIONAL FEE (37 CFR 1.492(A)(1) - (5)):

Search Report has been prepared by the EPO or JPO \$860.00

International preliminary examination fee paid to USPTO (37 CFR 1.482)
..... \$690.00No international preliminary examination fee paid to USPTO (37 CFR 1.482)
but international search fee paid to USPTO (37 CFR 1.445(a)(2)) ... \$710.00Neither International preliminary examination fee (37 CFR 1.482) nor
international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$1000.00International preliminary examination fee paid to USPTO (37 CFR 1.482)
and all claims satisfied provisions of PCT Article 33(2)-(4) \$100.00

ENTER APPROPRIATE BASIC FEE AMOUNT =

\$860.00

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(e)).

\$ 0

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
Total claims	17 - 20 = 0	0	x \$18.00
Independent	1 - 3 = 0	0	x \$80.00
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$250.00

\$ 0

\$ 0

\$ 0

TOTAL OF ABOVE CALCULATIONS =

\$860.00

Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement
must also be filed (Note 37 CFR 1.9, 1.27, 1.28).

\$ 0

SUBTOTAL =

\$860.00

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(f)).

\$ 0

TOTAL NATIONAL FEE =

\$860.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property

\$ 40.00

TOTAL FEES ENCLOSED =

\$900.00

Amount to be:
refunded

\$

charged

\$

- a. ☒ A check in the amount of \$900.00 to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No. 50-0624 in the amount of \$_____ to cover the above fees.
A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit
Account No. 50-0624. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a)
or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Norman D. Hanson
FULBRIGHT & JAWORSKI L.L.P.
666 Fifth Avenue
New York, NY 10103

SIGNATURE

Norman D. Hanson July 31, 2001
NAME30,946
REGISTRATION NUMBER

09/890544

JC05 Rec'd PCT/PTO 31 JUL 2001

CERTIFICATE OF EXPRESS MAIL

"Express Mail" mailing label # EL 649537808 US

Date of Deposit July 31, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service on the date indicated above and is addressed to: Commissioner of Patents and Trademarks, Washington D.C. 20231

Annette Crossan

(Name of Depositor)

Annette Crossan

(Signature of Depositor)

09890544-07101

Fulbright & Jaworski L.L.P.
666 Fifth Avenue
New York, New York 10103

09/890544

JCO5 Rec'd PCT/PTO 31 JUL 2001

EXPRESS MAIL LABEL #EL649537808US

I hereby certify that this correspondence is being deposited with the United States Postal Service as Express Mail in an envelope addressed to Commissioner, of Patents and Trademarks, Washington, D.C. 20231 on July 31, 2001.

Janette Crosson

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants : Thalhammer, et al.

Serial No. : Please assign

Filed : Herewith

For : PROCESS FOR PREPARING SODIUM
DICYANAMIDE

Based on : PCT/EP00/00900

International Filing Date : February 4, 2000

July 31, 2001

Hon. Commissioner of Patents
and Trademarks
Washington, D.C. 20231

**PRELIMINARY
AMENDMENT**

SIR:

Prior to examination, please amend this application as follows:

IN THE SPECIFICATION:

Page 3, line 36: after "cyanamide" add -- in aqueous solution --

Lines 37-38: delete "in aqueous solution."

IN THE CLAIMS

Please amend claims 1 and 3-14, and add claims 15-17, as follows:

1. A process for preparing sodium dicyanamide [which comprises] comprising
[cyanamide being reacted] simultaneously reacting cyanamide in aqueous solution

For the PTO

with a sodium hydroxide solution and cyanogen chloride [in aqueous solution], at a temperature[s] of from 40°C to 100°C, and at a pH of from 7.0 to 10.0.

3. The process as claimed in claim 1 [or 2] wherein the sodium hydroxide solution is used as a 10% to 50% by weight aqueous solution [, preferably a 20 to 30% by weight solution].
4. The process as claimed in [one of claims] claim 1 [to 3] wherein cyanogen chloride is used in the gaseous state and in technical grade quality.
5. The process as claimed in [one of claims] claim 1 [to 4], wherein the reaction temperature is 50 to 80°C.
6. The process as claimed in [one of claims] claim 1 [to 5], wherein the pH is set [to] at from 7.0 to 8.5.
7. The process as claimed in [one of claims] claim 1[to 6], wherein 2.0 to 2.4 mol of sodium hydroxide are used per mole of cyanamide.
8. The process as claimed in [one of claims] claim 1 [to 7], wherein the cyanogen chloride is used at an equimolar, or approximately equimolar, ratio based on the cyanamide used.
9. The process as claimed in [one of claims] claim 1 [to 8], wherein the [raw materials] cyanamide, sodium hydroxide and cyanogen chloride are metered [separately simultaneously] to a reactor separately but simultaneously [with good] while mixing, continuously and [the] reaction solution is [taken off] removed continuously.
10. The process as claimed in [one of claims] claim 1 [to 9] comprising metering [wherein] the cyanogen chloride [is metered in such a manner that a] while maintaining a constant pH [is maintained].
11. The process as claimed in [one of claims] claim 1 [to 10] wherein [the raw materials] cyanamide, sodium hydroxide and cyanogen chloride are used at [a concentrate] concentrations such that the sodium dicyanamide produced remains completely in solution at the [respective] reaction temperature used.

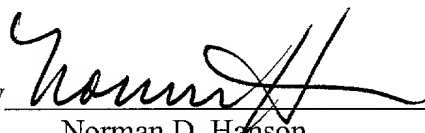
12. The process as claimed in [one of claims] claim 1 [to 11], comprising crystallizing the sodium dicyanamide [is crystallized] out of the reaction solution and separating it therefrom [separated off by customary methods, for example filtration].
13. The process as claimed in [one of claims 1 to] claim 12 comprising [wherein] treating the reaction solution with activated carbon before [the crystallization] crystallizing the sodium dicyanamide [is subjected to a treatment] [with activated carbon].
14. The process as claimed in claim 13, wherein the reaction is treated with 0.1g to 5.0g of activated carbon per liter of solution.
15. The process of claim 2, wherein the sodium hydroxide solution is used as a 10% to 50% by weight solution.
16. The process of claim 2, wherein the sodium hydroxide solution is used as a 20% to 30% by weight solution.
17. The process of claim 12, comprising separating said sodium dicyanamide by filtration.

REMARKS

Entry of the foregoing amendment is requested.

Respectfully submitted,

FULBRIGHT & JAWORSKI L.L.P.

By 
Norman D. Hanson
Reg. No. 30,946

666 Fifth Avenue
New York, New York 10103
(212) 318-3000

Process for preparing sodium dicyanamide

Description

- 5 The present invention relates to a preferably continuous process for preparing sodium dicyanamide which is suitable in particular for the industrial scale.
- 10 Sodium dicyanamide is used in large amounts for preparing biocidal active compounds in the sanitary and healthcare sectors and for disinfection in food production.
- 15 According to the prior art, various methods are used for preparing sodium dicyanamide. Thus, for example, CA Vol. 109, 218 568 (1988) describes the reaction of ammonia with cyanogen chloride and metal hydroxides at 20 to 30°C. This achieves a conversion rate of 90.5%
- 20 with a purity of 94.3%. However, this procedure is associated with some fundamental disadvantages. The low temperature level in the highly exothermic reaction requires the use of cooling brine and thus expensive electrical cooling energy. Since the space/time
- 25 conversion rate is determined primarily by the effectiveness of heat removal and, in the case of this process, furthermore a relatively large amount of heat of reaction is liberated, very high production costs because of the relatively large apparatuses and poor
- 30 heat balance must be expected. In addition, roughly twice the amount of cyanogen chloride and sodium hydroxide solution are consumed per mole of sodium dicyanamide in order to prepare the intermediate cyanamide. In addition, an equimolar amount of
- 35 contaminated sodium chloride is produced, which must be disposed of in a very costly manner, which appears problematic with respect to environmental aspects.

5 A general problem in the preparation of sodium dicyanamide is removing the by-product sodium chloride, since the two compounds are sodium salts with good solubility in water. A process in which twice the amount of sodium chloride is produced in a mixture with the target product thus also leads to considerably impaired yield of pure sodium dicyanamide.

10 The sodium dicyanamide purity required by active compound manufacturers is customarily at least 97% by weight, frequently even at least 98% by weight, which is not achieved by the process according to CA 109; 210 568 (1988).

15 A similar process is described in CA Vol. 110; 138 089 (1989), in which a solution of cyanogen chloride in benzene is charged and ammonia is added. The amount of cyanogen chloride charged and the use of organic solvent, in this case the carcinogenic benzene, make
20 this process impracticable on the industrial scale.

Canadian Patent 956 081 describes an alternative synthetic pathway for sodium dicyanamide, starting from cyanamide, sodium cyanide and chlorine, with addition
25 of sodium hydroxide solution.

From the reaction equation it is clear that, in this process also, two moles of sodium chloride are formed per mole of sodium dicyanamide, with the result that
30 the separation problems already described above occur with adverse consequences on product purity and yield. Although the process gives conversion rates of > 96%, isolated yields of 73 to 78% are obtained at a purity of 73 to 86% by weight. This reflects the difficulty of
35 the sodium chloride removal which has been discussed. From the aspect of raw material and disposal costs, this process is also disadvantageous, since the raw materials sodium cyanide and chlorine used are

09090544 073101

The object underlying the present invention, therefore, was to develop a process for preparing sodium dicyanamide which does not have said disadvantages corresponding to the prior art, but which permits sodium dicyanamide to be prepared from inexpensive raw materials which are available on an industrial scale and thus meets the stringent requirements of safety and product purity.

It has surprisingly been found here that an extremely
20 pure sodium dicyanamide can be obtained in very good
yields even with the use of technical-grade raw
materials. This was surprising because the process can
be carried out even at elevated temperature conditions
without disadvantageous effects on purity of the
25 product and selectivity of the reaction and it is known
to those skilled in the art that under the claimed
reaction conditions, usually cyanamide is very rapidly
dimerized and cyanogen chloride is very rapidly
hydrolyzed to cyanate by sodium hydroxide solution.
30 Against this background, among those skilled in the art
there was the prejudice for keeping the reaction
temperature as low as possible for reactions with
cyanogen chloride in aqueous alkali media.

35 In the process according to the present invention, cyanamide is simultaneously reacted with sodium hydroxide solution and cyanogen chloride in aqueous solution. The choice of cyanamide as raw material means that in the reaction only 1 equivalent of sodium

chloride is produced as by-product. Preferably, cyanamide is used in the form of a 20 to 60% by weight aqueous solution, in particular in the commercially conventional concentration of 50% by weight (SKW cyanamide L500) and the sodium hydroxide solution is used as 10 to 50% by weight aqueous solution, in particular 20 to 30% by weight solution. If the concentration of cyanamide is decreased, it is advantageous to increase the content of sodium hydroxide solution, and vice versa.

The product concentration can be controlled as desired by the concentration of the raw materials cyanamide and sodium hydroxide solution. Thus, preferably, raw material concentrations are used from which, without evaporation or dilution operations, a product concentration results at which the reaction product remains completely in solution and from which, during the crystallization, sodium dicyanamide crystallizes out to the greatest possible extent, but the stoichiometric by-product sodium chloride does not yet crystallize out. However, in principle, it is possible to choose the concentrations of these reaction components independently and as desired, if the abovementioned advantage of a direct crystallization of the product is not intended or if the reaction mixture is set later to the desired concentration by concentration or dilution.

Cyanogen chloride may preferably be used according to the inventive process as a technical-grade gas, which is of critical importance both for the economic efficiency and for plant safety. Firstly, in contrast to the use in condensed or dissolved form, the holdup in a plant can be kept extremely low, even for an industrial scale production, and thus hazard to personnel and environment can be virtually excluded. In the case of gaseous cyanogen chloride, in contrast to condensed or highly concentrated solutions, there is

also not the risk of a spontaneous highly exothermic trimerization.

5 Technical-grade cyanogen chloride also comprises minor components in the range from 3 to 8% by volume, for example carbon dioxide or chlorine. In this case also, it has surprisingly been found that these minor components lead to completely harmless products, which are not present in the isolated sodium dicyanamide.

10 It is considered an important advantage of the inventive process that the reaction, in contrast to the prior art, can be carried out even at elevated temperature, in particular at 40 to 80°C, without side
15 reactions occurring to an increased extent in this case. This has critical consequences from the ecological and process-engineering aspects. Firstly, the great exothermy of the reaction is utilized to heat the reaction parameters added cold; secondly, the
20 excess heat can be simply removed via a heat exchanger using cold water. In the processes corresponding to the prior art, the temperature gradient of reaction solution to cooling water is not sufficient for an economic procedure, so that electrical cooling energy
25 must be employed.

When the inventive reaction is carried out, it has proved to be particularly advantageous to control the amounts of reaction participants in a targeted manner.
30 This is because it has been found in this case that the reaction and also the following process steps proceed optimally if a defined stoichiometric ratio is maintained during each phase of the metering. The metering of sodium hydroxide solution and cyanamide is
35 preferably implemented by a rate measurement, as a function of the concentration of these raw materials. In this case the ratio of the reactants is preferably set in such a manner that 2.0 to 2.4 mol, preferably 2.1 to 2.2 mol, of sodium hydroxide are used per mole

of cyanamide. The exact ratio is dependent on the purity of the cyanogen chloride used.

Exact and reliable rate-controlled metering of gaseous industrial-grade cyanogen chloride is extremely difficult from the metrological aspect. Conventional apparatuses for flow metering are of little use in practice. For this reason, preferably, cyanogen chloride is added under pH control in such a manner that in the reaction solution a pH of 7.0 to 10.0, preferably 7.0 to 8.5, is maintained. At this pH, the reaction partners react immediately in the desired manner. At a lower pH there is the risk that the extremely toxic cyanogen chloride is not reacted completely to exhaustion and is released during work-up. At higher pHs, side reactions such as hydrolysis of cyanogen chloride and dimerization of cyanamide occur to an increased extent. Generally, cyanogen chloride is used in an equimolar, or approximately equimolar, ratio based on the cyanamide used. According to a preferred embodiment, the raw materials are metered in separately simultaneously to a reactor with good mixing and the reaction solution is taken off continuously. Although prior mixing of cyanamide and sodium hydroxide solution, or cyanamide and cyanogen chloride, is possible in principle, it has disadvantages with respect to product quality or process safety.

By means of the simultaneous metering of the raw materials into a reactor (for example a residence-time reactor) with good mixing, the same concentration, temperature and pH conditions are always present during the entire course of the reaction. This leads to two important beneficial effects, that is to say, firstly, minimizing unwanted by-products, for example dicyanodiamide and sodium N-cyanoisourea, which inhibit a clean selective crystallization of the product and are themselves difficult to remove. Secondly, as a result, the dimensions of the reactor, the heat

exchanger and other apparatuses can be reduced, which leads to considerable savings in capital costs and maintenance. Suitable reactors are, for example, recirculation reactors equipped with static mixers or
5 mixing nozzles or tubular reactors having gas-introduction agitators.

Following the reaction, sodium dicyanamide can be crystallized out in very high purity from the hot
10 reaction solution directly by targeted crystallization either batchwise or via a controlled cooling curve or a continuous crystallizer. If the procedure starts from technical-grade raw materials, the reaction solution can still contain small amounts of discoloring
15 impurities, which are generally not of high-molecular-weight nature.

According to a preferred embodiment, this discoloration can be effectively eliminated by treatment with
20 activated carbon, even in very low amounts. For this, the product solution is admixed hot with 0.1 to 5 g of activated carbon per liter and the carbon is removed again in a conventional manner before the crystallization. Alternatively, the solution can also
25 be run through an activated carbon bed or filters prepared with activated carbon.

An important advantage of the present invention must be considered to be the fact that, despite a high
30 concentration, the product is maintained dissolved in the reaction solution, or is brought completely into solution by further heating to, for example, 60 to 100°C.

35 Starting from this solution, by controlled cooling, selective crystallization of sodium dicyanamide can be achieved, while the stoichiometric by-product sodium chloride remains in solution. Crystallization proceeds uniformly without formation of cocrystals or

09890544-073101
TOP SECRET

inclusions, so that complex recrystallization of the product or other work-up is not required. Selective crystallization of sodium dicyanamide is also possible by controlled continuous addition of hot sodium

5 dicyanamide solution to a cooled product suspension, or by concentration from dilute solutions, if appropriate with simultaneous cooling. It is critical in this case that the solution does not fall below the solubility curve of sodium chloride.

10

Sodium dicyanamide is isolated then in a customary manner by filtration, with adherent residual mother liquor being able to be removed by careful washing with water.

15

Using the inventive process it is possible, starting from raw materials available in technical-grade quality, to prepare sodium dicyanamide in a very environmentally friendly manner in good yields of

20 approximately 75 to 95% and very high purities of up to 100%, for which reason this process is particularly highly suitable for the industrial scale.

25

The examples below are intended to illustrate the invention in more detail.

Examples

Example 1

5 A 2.5 l recirculation reactor equipped with temperature
and pH measurement, heat exchanger and metering system
having a static mixer was operated continuously. The
metering system consisted of a glass tube in the
10 reactor circuit having separate ports for cyanamide,
sodium hydroxide solution and cyanogen chloride.
Immediately downstream of these metering ports was a
mixing section (\varnothing 1.6 cm, length 5 cm) containing
Sulzer mixing elements. The mean circulation rate was
14 l/min. At the start, the reactor was charged with
15 water at 60°C and then metering of the raw materials
was started.

The following amounts were added per hour via
peristaltic pumps:

20

Raw material	Concentration	Amount/h	Mol/h
Cyanamide	50.1%	515 g	6.13
Sodium hydroxide solution	28.0%	1 857 g	13.00

Technical-grade cyanogen chloride was introduced
simultaneously in the gaseous state in such a manner
that a pH of 7.5 to 8.0 was maintained. The consumption
25 was determined at 370 g/h (6.02 mol/h) based on pure
substance. At this metering rate a mean residence time
of 1 hour 35 minutes in the reactor resulted. The heat
exchanger was charged with enough cooling water to set
a reaction temperature of 70 to 75°C. The volumes
30 metered in were taken off via a free overflow and
passed through a bed containing powdered activated
carbon (10 g per 15 l of reaction solution) into a
buffer vessel. The buffer vessel was kept at 75°C
during charging and then cooled to 0°C in the course of
35 7.5 hours using a linear cooling curve. By alternately

filling two buffer vessels, the reaction could be conducted continuously. After crystallization, the product was filtered off using suction and washed with 500 ml of ice water per kg of filter cake.

5 Sodium dicyanamide was obtained at a purity of 100% without detectable contamination with dicyandiamide or sodium N-cyanoisourea, and with a chloride content of 0.2%. The APHA value (discoloration) of a 10% strength solution in water was 10. The yield isolated was 76%,
10 based on cyanamide used.

Example 2

15 In a similar manner to Example 1, sodium dicyanamide was prepared continuously in the apparatus described except that the reaction solution was not filtered through activated carbon. The sodium dicyanamide isolated had a purity of 99% without detectable contamination with dicyandiamide or sodium N-cyanoisourea, and with a chloride content of 0.6%.
20 The APHA value (discoloration) of a 10% strength solution in water was 55.

Example 3

25 A recirculation reactor system having a total volume of 4.2 l, consisting of a double-jacketed glass vessel, a diaphragm recirculation pump and a metering system for the raw materials was operated continuously to prepare
30 sodium dicyanamide. The metering system consisted of a driving jet nozzle operated with reaction solution, which drew in gaseous cyanogen chloride and mixed it with the reaction partners cyanamide and sodium hydroxide solution which were metered in immediately at
35 the nozzle exit via peristaltic pumps. Via the lid of the glass vessel, a free overflow led into a buffer vessel heated to 70°C. In the glass vessel temperature and pH were monitored and the metering of the raw materials was controlled accordingly. The amount

circulated was taken off from the bottom of the reactor and brought to the pressure of 1.4 bar which was required for the driving jet by means of a diaphragm pump. To even out the pressure, an equilibration vessel
5 was connected between pump and driving jet nozzle. This experimental arrangement was operated with the following parameters:

- Circulation rate: 210 l/hour
- 10 Constant molar ratio of sodium hydroxide to cyanamide = 2.18
- Concentration of cyanamide: 50.0%
- Concentration of sodium hydroxide solution: 28.0%
- 15 Temperature in the recirculation reactor: 70 to 75°C
- Nozzle pressure: 1.4 bar
- pH: 7.2 - 8.0
- 20 Metering rates:
- Cyanamide: 925 g/hour = 11.01 mol/hour
- Sodium hydroxide solution: 3430 g/hour = 24.01 mol/hour
- Cyanogen chloride (96% pure): 705 g/hour = 11.01 mol/hour
- 25 At the start, the recirculation reactor was filled with water at 70°C and the circulation rate was set. The raw material metering was then started, with the cyanogen chloride rate being controlled in such a manner that the internal temperature, under external cooling with
- 30 cooling water (18°C), remained in the range 70 to 75°C. The liquid components cyanamide and sodium hydroxide solution were fed at a constant molar ratio via controllable peristaltic pumps under pH monitoring. Via the free overflow, the product solution was collected
- 35 in the buffer vessel and after it was filled, drained off into an agitated crystallization vessel. The solution was cooled to 0°C in the course of 4 hours via a linear cooling curve and the product was isolated by filtration on a vacuum filter funnel. The product was

09090544-0340
FOI E.O. 14176

washed with 500 ml of ice water per kg of filter cake and dried under reduced pressure at 60°C.

In this manner, 803 g (= 82% of theory) of sodium dicyanamide at a purity of 98.5% were obtained per
5 hour. The sole impurity present at > 0.1% was sodium chloride at 1.3%.

Example 4

10 In a similar manner to Example 3, a sodium dicyanamide solution was prepared continuously, but, downstream of the free overflow, this was run out of the reactor system directly into a product suspension charged into
15 the buffer vessel and cooled to 0°C. After the buffer vessel was filled, this was emptied down to a remainder of approximately 1 liter and filled again without interruption. The sodium dicyanamide suspension take off was filtered in the usual manner, the filter cake was washed and dried.
20 814 g (= 83% of theory) of sodium dicyanamide at a purity of 98.3% were obtained per hour.

Example 5

25 In a similar manner to Example 3, sodium dicyanamide was prepared, but the filter cake was not washed during the product isolation. 920 g/hour (= 94% of theory) of sodium dicyanamide at a purity of 94.8% were obtained. The product comprised 4.8% of sodium chloride and 0.18%
30 of sodium N-cyanoisourea.

Example 6

Sodium dicyanamide was prepared in accordance with
35 Example 3, except that in the reaction part a temperature of 50 to 55°C was maintained, whereas in the buffer vessel a temperature of 90°C was set. Because of the low temperature level for the same

cooling area, in this experiment the following amounts could be metered per hour:

- 823 g (9.8 mol) of cyanamide (50% strength)
- 3050 g (20.4 mol) of sodium hydroxide solution
5 (28% strength)
- 608 g (9.5 mol) of cyanogen chloride (96% strength)

During the reaction, crystals had already formed, which redissolved in the heated buffer vessel, however. After
10 the corresponding work-up, 690 g/hour (79% of theory) of sodium dicyanamide at a purity of 97.6% were obtained.

Example 7

15

Sodium dicyanamide was prepared continuously in accordance with Example 6, except that a 15% by weight sodium hydroxide solution was used. The following amounts were metered per hour in this case:

20

- 820 g (9.8 mol) of cyanamide (50% strength)
- 5700 g (20.4 mol) of sodium hydroxide solution
(15% strength)
- 600 g (9.4 mol) of cyanogen chloride (96% strength)

A reddish-brown solution was obtained which was run
25 through an activated carbon bed (1 g per liter of solution) at 55°C, at a residence time of 10 min. The filtered solution was then evaporated under reduced pressure (approximately 200 mbar) until a thin crystal slurry was formed at 60°C. This slurry was cooled in a
30 linear manner to 0°C in the course of 3 hours and the product isolated in the usual way.

730 g (87% of theory) of sodium dicyanamide at a purity of 97.2% were obtained per hour. The sodium chloride content in the product was 2.4%.

35

Patent Claims

1. A process for preparing sodium dicyanamide, which comprises cyanamide being reacted simultaneously with sodium hydroxide solution and cyanogen chloride in aqueous solution at temperatures of 20 to 100°C and a pH of 7.0 to 10.0.
2. The process as claimed in claim 1, wherein cyanamide is used as a 20 to 60% by weight aqueous solution.
3. The process as claimed in claim 1 or 2, wherein the sodium hydroxide solution is used as a 10 to 50% by weight aqueous solution, preferably a 20 to 30% by weight solution.
4. The process as claimed in one of claims 1 to 3, wherein cyanogen chloride is used in the gaseous state and in technical-grade quality.
5. The process as claimed in one of claims 1 to 4, wherein the reaction temperature is 50 to 80°C.
6. The process as claimed in one of claims 1 to 5, wherein the pH is set to 7.0 to 8.5.
7. The process as claimed in one of claims 1 to 6, wherein 2.0 to 2.4 mol of sodium hydroxide are used per mole of cyanamide.
8. The process as claimed in one of claims 1 to 7, wherein the cyanogen chloride is used an equimolar, or approximately equimolar, ratio based on the cyanamide used.
9. The process as claimed in one of claims 1 to 8, wherein the raw materials are metered in separately simultaneously to a reactor with good

mixing and the reaction solution is taken off continuously.

- 5 10. The process as claimed in one of claims 1 to 9, wherein the cyanogen chloride is metered in in such a manner that a constant pH is maintained.
- 10 11. The process as claimed in one of claims 1 to 10, wherein the raw materials are used at a concentration such that the sodium dicyanamide remains completely in solution at the respective reaction temperature.
- 15 12. The process as claimed in one of claims 1 to 11, wherein the sodium dicyanamide is crystallized out of the reaction solution and separated off by customary methods, for example filtration.
- 20 13. The process as claimed in one of claims 1 to 12, wherein the reaction solution, before the crystallization, is subjected to a treatment with activated carbon.
- 25 14. The process as claimed in claim 13, wherein the reaction solution is treated with 0.1 to 5 g of activated carbon per liter of solution.

030044 0340
T07E'0" +4506360

Abstract

A process is described for preparing sodium dicyanamide, in which cyanamide is reacted simultaneously with sodium hydroxide solution and cyanogen chloride in aqueous solution at temperatures of 20 to 100°C and a pH of 7.0 to 10.0. By means of the inventive process it is possible, starting from raw materials which are available in technical-grade quality, to prepare sodium dicyanamide in good yields of 75 to 95% and very high purities of up to 100% in a very environmentally friendly manner, for which reason this process is particularly highly suitable for the industrial scale.

0990344 03.03

PTO/SB/01 (4-96)

Approved for use through 9/30/98 OMB 0651-0032

Type a plus sign (+) inside this box → ☐

Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE

DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION

☐ Declaration Submitted with Initial Filing OR ☐ Declaration Submitted after Initial Filing

Attorney Docket Number

First Named Inventor

COMPLETE IF KNOWN

Application Number

Filing Date

Group Art Unit

Examiner Name

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Process for preparing sodium dicyanamide

(Title of the Invention)

the specification of which

☐ is attached hereto
OR

☒ was filed on (MM/DD/YYYY) February 04, 2000 as United States Application Number or PCT International

Application Number PCT/EP00/00900 and was amended on (MM/DD/YYYY) July 14, 2000 / February 12, 2001 (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code §119 (a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365 (a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached?	
				YES	NO
199 04 877.0	DE	Feb. 06 99	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

☐ Additional foreign application numbers are listed on a supplemental priority sheet attached hereto.

I hereby claim the benefit under Title 35, United States Code §119(e) of any United States provisional application(s) listed below.

Application Number(s)	Filing Date (MM/DD/YYYY)	<input type="checkbox"/> Additional provisional application numbers are listed on a supplemental priority sheet attached hereto.

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Burden Hour Statement: This form is estimated to take 0.4 hours to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, Patent and Trademark Office, Washington, DC 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner of Patents and Trademarks, Washington, DC 20231.

(July 1996)

PTO/SB/01 (12-97)

Approved for use through 9/30/00. OMB 0651-0032

Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Please type a plus sign (+) inside this box ☐

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

DECLARATION — Utility or Design Patent Application

I hereby claim the benefit under 35 U.S.C. 120 of any United States application(s), or 365(c) of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of 35 U.S.C. 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

U.S. Parent Application or PCT Parent Number

Parent Filing Date (MM/DD/YYYY)

Parent Patent Number (if applicable)

☐ Additional U.S. or PCT international application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto.

As a named inventor, I hereby appoint the following registered practitioner(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith: ☐ Customer Number ☐ OR ☐ Registered practitioner(s) name/registration number listed below

Place Customer Number Bar Code Label here

Name

Registration Number

Name

Registration Number

☐ Additional registered practitioner(s) named on supplemental Registered Practitioner Information sheet PTO/SB/02C attached hereto.Direct all correspondence to: ☐ Customer Number ☐ OR ☐ Correspondence address below

Name

Fulbright & Jaworski L.L.P.

Address

666 Fifth Avenue

Address

New York, N.Y. 10103

City

New York

State

NY

ZIP

10103

Country

USA

Telephone

001-212-3183000

Fax

001-212-7525958

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name of Sole or First Inventor:

☐ A petition has been filed for this unsigned inventor

Given Name (first and middle (if any))

Family Name or Surname

Franz

THALHAMMER

Inventor's Signature

X *F. Thallhammer*

Date

8/6/00

Residence: City

83308 Trostberg

State

Country

Germany

Citizenship

DE

Post Office Address

Kolpingstraße 13, 83308 Trostberg, Germany

Post Office Address

City

State

ZIP

Country

☒ Additional inventors are being named on the supplemental Additional Inventor(s) sheet(s) PTO/SB/02A attached hereto

Type a plus sign (+) inside this box → ☐

DECLARATION

ADDITIONAL INVENTOR(S)
Supplemental Sheet

Name of Additional Joint Inventor, if any:				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name	Helmut	Middle Initial		Family Name	TAUTZ	Suffix e.g. Jr.	
Inventor's Signature	X T E				Date	X 25.06.2001	
Residence: City	93326 Abensberg	State		Country	Germany	Citizenship	DE
Post Office Address	Ludwig-Berger-Straße 19, 93326 Abensberg, Germany						
Post Office Address							
City		State		Zip		Country	
Name of Additional Joint Inventor, if any:				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name		Middle Initial		Family Name		Suffix e.g. Jr.	
Inventor's Signature					Date		
Residence: City		State		Country		Citizenship	
Post Office Address							
Post Office Address							
City		State		Zip		Country	
Name of Additional Joint Inventor, if any:				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name		Middle Initial		Family Name		Suffix e.g. Jr.	
Inventor's Signature					Date		
Residence: City		State		Country		Citizenship	
Post Office Address							
Post Office Address							
City		State		Zip		Country	
Name of Additional Joint Inventor, if any:				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name		Middle Initial		Family Name		Suffix e.g. Jr.	
Inventor's Signature					Date		
Residence: City		State		Country		Citizenship	
Post Office Address							
Post Office Address							
City		State		Zip		Country	
Name of Additional Joint Inventor, if any:				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name		Middle Initial		Family Name		Suffix e.g. Jr.	
Inventor's Signature					Date		
Residence: City		State		Country		Citizenship	
Post Office Address							
Post Office Address							
City		State		Zip		Country	
<input type="checkbox"/> Additional inventors are being named on supplemental sheet(s) attached hereto							

FOIEU 44506860